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Diameter sensitive effect in singlewalled carbon nanotubes upon acid treatment

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ABSTRACT

Singlewalled carbon nanotubes (SWCNT) exhibit very unique properties. As an electronic system they undergo amphoteric doping effects (n-type and p-type) which can be reversed. These processes affect the optical and vibronic properties of the carbon nanotubes. The most common and widely used procedure which changes the properties of the SWCNT is acid treatment applied as a purification procedure. This effect has been widely studied but not fully understood so far. Here, we present a study, in which a diameter sensitive effect has been observed. Therefore, two kinds of SWCNT samples have been studied: (i) produced via chemical vapour deposition with a broad diameter distribution, and (ii) synthesised by the laser ablation technique which is commonly known to result in narrow diameter distribution bulk SWCNT samples. Resonance Raman spectroscopy, optical absorption spectroscopy, and Fourier transform middle-infrared spectroscopy have been applied for the characterisation of the samples.

1. Introduction

Carbon nanotubes (CNT) have been investigated very intensely over the last years. Singlewalled carbon nanotubes (SWCNT), in particular, are currently the aim of research investigations due to their multiple interesting properties. SWCNT can be synthesised by different routes, being the most used arc discharge, laser ablation (LA), and chemical vapour deposition (CVD) [1]. When a metallic catalyst is required for the synthesis process the sample purity becomes a problem and further purification steps are mandatory in order to remove the catalyst particles. To obtain the bulk scale purity, acid treatments have often been reported e.g. nitric acid reflux [2–4]. However, this procedure leads to the formation of functionalised products in which the electronic properties are modified as molecules can penetrate the graphite layer, generating defects and charge transfer [5]. A characteristic behaviour of SWCNT is that they form bundles due to Van der Waals inter-tube bonding [6–9]. When the dopant molecules are intercalated into the SWCNT bundles an expansion of the inter-tube spacing causing changes in the diameter of the nanotubes can be observed. Kukovecz et al. have shown that the doping process is diameter selective and that the graphite lattice can expand to accommodate the molecules of the dopant [5]. To follow this behaviour in greater detail, spectroscopic studies, such as resonance Raman response and optical absorption spectroscopy (OAS), have been carried out. The Fourier transform infrared technique was employed to detect the formation of new functional groups on the surface of the nanotubes upon the acid treatment. These tools are very powerful to understand the changes occurring in the optical and vibronic properties of the functionalised SWCNT in respect to the pristine material [10–13]. Many efforts have been made to understand these modifications. Nevertheless, the full understanding of this field still remains a challenge. The importance of this study comes from the fact that carbon nanotubes are now being widely considered for medical applications and the acid purified samples are often used for further bio-functionalisation. Therefore, a better understanding of the influence of the purification procedure on the SWCNT properties is still essential.

Here, we present a study on concentrated acid treated SWCNT which leads to a shortening of the C–C bonds in the carbon nanotube structure, and to a Fermi level shift which is reflected in drastic changes in the radial breathing mode region and in the response of the carbon nanotubes, respectively. These findings are observed for the selected tube diameters.

2. Experimental

In the current work two different samples of SWCNT were studied. The first batch of SWCNT was produced by the CVD process (CVD-S1) [14]. The characteristic property of this sample is a broad diameter distribution (0.82–1.87 nm). The second batch of SWCNT was synthesised by a standard laser ablation technique [15,16], with a narrow diameter distribution (LA-S2 (1.22 ± 0.16 nm)). As a first purification step the samples were annealed in air at 300 °C. Afterwards, the annealed samples were refluxed for 24 h in acid solution of diluted *aqua regia* composed of a mixture of (HNO_3:HCl):H_2O with a ratio of (1:3):4. Finally, the samples were filtered with a microfiltration system, and washed with distilled water and acetone. In order to remove any functional groups formed on the nanotube surface an annealing procedure in high vacuum (10^{-5} mbar) at 800 °C was performed. A Renishaw in via Raman microscope spectrometer ($\lambda = 785$ nm), a Jasco-570 UV–vis/NIR spectrophotometer,

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and a Nicolet-530 FTIR spectrophotometer were used. The samples were prepared by dispersing the products in acetone followed by a sonication step until a homogeneous suspension was reached. Subsequently, the suspension was dropped onto a heated KBr crystal (ca. 100 °C). This procedure was repeated for pristine, purified and annealed samples. A typical SWCNT Raman spectrum contains the tangential mode G-band, which is reminiscent of in-plane modes in graphite, the disorder induced D-band, and the radial breathing mode (RBM), through which it is possible to calculate the diameter of the tubes [17]. The UV–vis/NIR spectra of SWCNT usually reveal the so called van Hove singularities (vHSs). The peaks observed are related to transitions between the densities of states (DOS) singularities in semiconducting and metallic tubes [18].

3. Results and discussion

SWCNT have amazing electronic properties. By the introduction of electron donor molecules, referred to as n-type doping (e.g. K), or electron acceptor as p-type doping (e.g. Br_2), into the hollows of the triangular SWCNT lattice, the Fermi level can be shifted resulting in modification of the properties without generating defects in the SWCNT bond network [5]. In our study, the dopant molecules (HCl and HNO_3) are electron acceptors, and charge transfer from the SWCNT to the acceptor molecule is expected. Therefore, a shortening of the C–C bond which leads to upshifts in Raman modes e.g. in RBM features [1], can result. The RBM is composed of many features corresponding to the atomic vibration of the C atoms in the radial direction as if the tube was breathing. This mode is carbon nanotube diameter sensitive and it is very useful for the characterisation of the nanotube diameters up to 2 nm [17].

The resonance in Raman intensity depends on the density of electronic states available for the optical transitions, and this property is very important for one-dimensional (1D) systems, such as SWCNT. An observable Raman signal from a carbon nanotube can be obtained when the laser excitation energy is equal to the energy separation between vHSs in the valence and conduction bands, but only for allowed electronic transitions [17]. Therefore, the different laser energies result in different nanotube excitations, since their electronic structure varies with their chirality and diameter distribution. Under different excitation energies different types of nanotubes are in resonance. Here, the laser wavelength of 785 nm corresponds to the energy of 1.58 eV, and only carbon nanotubes with this value of the energy separation between vHSs will give a Raman response. All the Raman spectra were normalised at ca. 300 cm^{-1}.

In Fig. 1a, the RBM spectra of the sample CVD-S1 before (solid line), after acid treatment (dashed line), and the acid treated sample after the annealing (dotted line) are presented. This sample exhibits a very wide diameter distribution, from 0.82 nm to 1.87 nm. Here, one can observe two effects for the acid treated specimen: (i) a decrease of the intensity of all the components in general, and (ii) an upshift of the RBM modes of the acid treated sample in respect to the pristine one. For the lower wavenumber region an upshift of 17 cm^{-1} was found. This gradually dropped to about 8 cm^{-1} at 182 cm^{-1}, and to only ca. 2 cm^{-1} for the remaining RBM components at 204 cm^{-1}. In the case of the acid treated CVD-S1 sample, after the annealing process, the RBM position was almost fully reversed to its initial position, although a slight downshift of the position only in the lowest wavenumber region was observed (see dotted line in Fig. 1a). The intensity of the components of the RBM modes increased significantly but the total intensity of the starting material was not reached. Fig. 1b represents the curve of the Raman upshift of the RBM components of the acid treated sample versus the corresponding carbon nanotube diameters. It can easily be observed that the strongest shift occurs for tube diameters of 1.62 nm up to 1.87 nm. The shift gradually decreases with decrease in tube diameter, being less for the tubes with diameter of 1.36 nm and not very significant for tubes with diameter below 1.21 nm. Keeping in mind that the cocktail of nanotubes with a broad diameter distribution went into resonance here, it was possible to observe diameter sensitivity to the doping effects. Two important effects explain the upshifts in the Raman spectra: (i) the charge transfer from the nanotubes to the dopant molecules, and a consequence shortening of the C–C bonds [1], and (ii) an increase on the thickness of the SWCNT bundles [5], caused by the intercalation of the dopant molecules into the interstitial channels. Both effects are proportional to the diameter of the nanotubes. The reduction of the intensity of the RBM modes for the selected tubes has already been reported for the case of K and $FeCl_3$ doped HiPCO SWCNT [19]. The observation was explained as a diameter selective doping process. The inter-tube channels in SWCNT bundles consisting of wider tubes are proportionally broader than those of thinner tubes. Therefore, the intercalation of the carbon nanotube cores and the interstitial channels is easier.

However, the second effect of the acid treatment – exohedral functionalisation, should also be considered. The defects on the nanotube walls become an active site for the formation of –COOH/–OH groups (see later in Fig. 4b). These functional groups also interact with the carbon walls which could result in the stronger upshift of the RBM components corresponding to the wider tubes. This interaction results in the contraction of C–C bonds in the nanotube structure and it is more pronounced for the tubes more affected by the acid treatment, therefore those with a higher amount of functional groups. In this way, the bigger upshift in the case of the wider tubes can be explained by the higher number

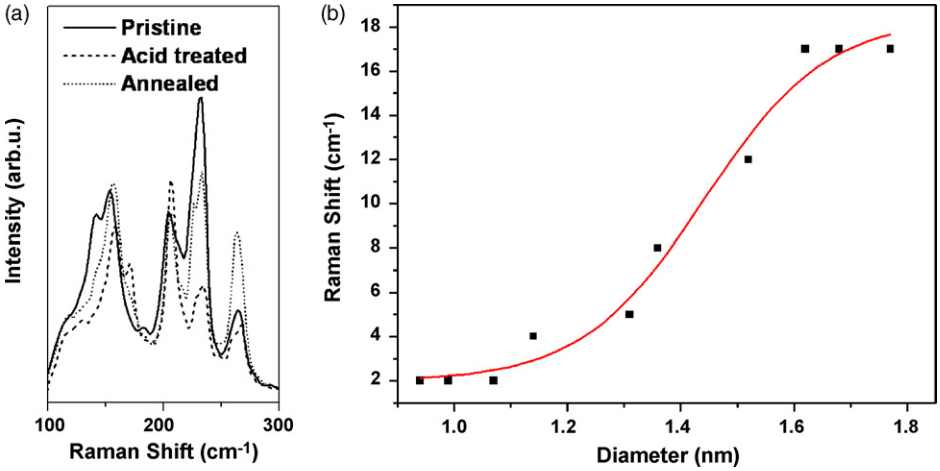

Fig. 1. (a) RBM feature in Raman spectrum of CVD-S1 sample; (b) relation between the diameter of nanotubes and their values of the shifts of RBM components in CVD-S1.